Supporting information

Synthesis of decyl selenocyanate (RSeCN)

A mixture of KSeCN and 1-bromodecane in the mole ratio of 1:1 was dissolved in dimethyl formamide (DMF) and allowed to stir for 16 h at 60° C. After the completion of the reaction, the resulting mixture was hydrolyzed and the compound was extracted into dichloromethane (DCM). The desired product was obtained after evaporating the organic layer. ¹H NMR (400 MHz, CDCl₃) δ 0.8 (t, 3H), 1.2 (m, 12 H), 1.37 (q, 2H), 1.8 (q, 2H), 3 (t, 2H); ¹³C NMR (CDCl₃) δ 102.1 (CN), 23.1, 29.3, 29.5, 29.7, 29.8, 29.9, 30.1, 31.3, 31.8, 32.3; ⁷⁷Se NMR (CDCl₃) 206.8.

Synthesis of didecyl Selenide (DDSe)

The above synthesized selenocyanate (3 mmol) was dissolved in warm ethanol and to which NaBH₄ (6 mmol) was added in proportions. The resulting mixture was stirred for 2 h at room temperature and later the mixture was hydrolyzed. The compound was extracted into DCM and the organic layer was washed with water. The crude product obtained after solvent evaporation was subjected to silica gel column chromatography. The desired product was eluted with pure hexane. ¹H NMR (400 MHz, CDCl₃) δ 0.88 (t, 6H), 1.3 (m, 24 H), 1.38 (q, 4H), 1.72 (q, 4H), 2.91 (t, 4H); ¹³C NMR (CDCl₃) δ 24.1, 28.6, 29.8, 30.0, 30.7, 32.4, 32.3; ⁷⁷Se NMR (CDCl₃) 159.4.



Fig. S0. (a) ¹H and (b) ¹³C NMR spectrums of didecyl selenium (RSeR).

Materials

Potassium selenocyanate (KSeCN), palladium (II) acetate, and Nafion (5 wt % solution in lower aliphatic alcohols /H₂O mixture) were procured from Aldrich, USA. Pt-loaded carbon 40 wt % Pt/C was purchased from Arora Matthey, India. 1-Bromodecane, sodium borohydrate (NaBH₄), potassium chloride (AnalaR grade) were obtained from Polysales, India and used as received. All solutions were prepared using water with resistivity 18.2 M Ω cm.

Synthesis of palladium selenides

Palladium-rich selenide phases were obtained by thermolysis of palladium organoselenolate complexes. The complexes with different compositions were prepared by mixing different mole ratios of palladium acetate and didecyl selenide (DDSe) in toluene (total volume of 2 mL) for 10 min under ambient conditions. In a typical synthetic procedure for the preparation of the complex, 40 μ L of DDSe and 50 mg of Pd(OAc)₂ were stirred for 10 min, under ambient conditions. The complexes are represented as B_{xy}, where x and y denotes the moles of Pd(OAc)₂ and DDSe respectively. The Se precursor (DDSe) was synthesized by adopting a reported procedure.¹¹ The complexes obtained by mixing the metal and selenium precursors were drop-casted on freshly cleaned glass slides of 1 cm² area and the solvent evaporated under ambient conditions. Subsequently, the thermal decomposition of the complexes was carried out in a tubular furnace at 250 °C for 1 h, under N₂ atmosphere resulting in the formation of stable, continuous and shiny black colored films.

Characterization - Structure, morphology, and composition

X-ray diffraction data were recorded using X'pert powder diffractometer (PANalytical, Inc.) with a Cu K α (1.54Å) X-ray source operated at 45 kV and 30 mA. Electron microscopy (SEM and TEM) of the films were performed with FESEM (Carl Zeiss ultra 55) equipped with EDX accessory and JEOL 2100F/FEI transmission electron microscope operating at 200 kV. The TEM samples were prepared by depositing the sample from an ethanolic dispersion using a micropipette on a carbon coated copper / holey carbon grid. High-resolution x ray photoelectron spectroscopy was carried out using Kratos Axis Ultra spectrometer (Kratos Analytical, Manchester, UK) equipped with a monochromated 1486.6 eV aluminum K α source. All the binding energies were referenced to carbon 1s level at 284.6 eV.

Electrochemical Studies

Electrochemical studies were performed using an electrochemical workstation CH660A with a conventional three-electrode arrangement comprising of palladium selenide films on glass slide or on toray carbon as the working electrode, large area Pt foil and saturated calomel electrode SCE, as counter and reference electrodes, respectively. The electrolyte used for HER study is $0.5M H_2SO_4$. Prior to the electrochemical measurements, the electrolyte was de-aerated by continuously purging with high purity N₂ gas for 30 min. The stability tests were carried out using Linear sweep voltammetry (LSV) at a scan rate of 100 mV s⁻¹ for 3000 scans. The electrochemical impedance spectra (EIS) were recorded in the frequency range of 100 KHz to 0.05 Hz with AC amplitude of 5 mV. The potentials are cited against reversible hydrogen electrode (RHE), whose value was obtained by calibrating SCE against RHE. In 0.5M H₂SO₄, E (RHE) = E (SCE) + 0.265 V (Fig. S1). Electrochemical accessible area of the catalysts can be calculated from under potential deposition of hydrogen

or metals. As it is known in the literature, hydrogen UPD is not seen in the case of palladiumbased catalysts. Therefore, Cu UPD experiments were carried out by employing chronoamperometric technique in 2 mM CuSO₄. $5H_2O$ solution, in nitrogen saturated 0.5M H_2SO_4 as supporting electrolyte. The potential was held at 0.25 V for 1 min to form monolayer Cu. To obtain the anodic Cu stripping cyclic voltammogram, the potential was scanned from 0.3 to 0.8 V and back to 0.3 V at a scan rate of 10 mV s⁻¹. CV was also recorded from 0 to 0.8 V in nitrogen saturated supporting electrolyte without CuSO₄ for background correction in calculating the surface area with the scan rate of 10 mV s⁻¹.



Fig. S1. (a) X-ray diffraction pattern of complex $[Pd(SeR_2)_2(OAc)_2]$ drop casted on glass slide. Inset shows the XRD pattern of $Pd(OAc)_2$.



Fig. S2. ⁷⁷Se NMR spectrum of complex Pd[(SeR₂)₂(OAc)₂]



Fig. S3. UV-Visible absorption spectra of (a) DDSe and $Pd(OAc)_2$, (b) complex B_{1y} formed by increasing selenium precursor content, (c) complex B_{x1} formed by increasing palladium precursor content.



Fig. S4. XRD patterns of (i) $Pd_{17}Se_{15}$, (ii) Pd_7Se_4 and (iii) Pd_4Se resulted from the thermal decomposition of B_{14} , B_{11} and B_{41} respectively.



Fig. S5. XRD patterns of different phases formed on thermal decomposition of complexes B_{xy} by varying the mole ratio of $Pd(OAc)_2$: DDSe. (a) represents mole ratios of 1:1 to 1:4 in the sequence (i) to (iv) and (b) represents mole ratios of 1:1 to 4:1 in the sequence (i) to (iv).



Fig. S6. (a), (b), (c) are SEM images of Pd₁₇Se₁₅, Pd₇Se₄ and Pd₄Se and (d), (e) and (f) are corresponding EDAX data.



Fig. S7. XPS survey spectrum of Pd₇Se₄ formed by thermolysis of the precursor complex.



Fig. S8. Resistivity as a function of temperature, for (a) Pd₇Se₄ and (b) Pd₄Se film.

In the case of $Pd_{17}Se_{15}$ phase, it is already reported to be metallic in nature. Reference 10 in the main text.



Fig. S9. Cyclic voltammograms of 10 mM $K_4[Fe(CN)_6]$ in 0.1M KCl on $Pd_{17}Se_{15}$ (i), Pd_7Se_4 (ii) and Pd_4Se (iii) films on a glass slide at a scan rate of 100 mVs⁻¹ and (b) Effect of scan rate on the voltammograms on $P_{17}Se_{15}$ film [inset shows linear fit of current density vs square root of scan rate].



Fig. S10. Cyclic voltammogram that shows the calibration of saturated calomel electrode (SCE) with respect to reversible hydrogen electrode (RHE). Scan rate used is 1 mVs⁻¹, in presence of H_2 saturated solution in 0.5M H_2SO_4 .



Fig. S11. (a) Linear sweep voltammograms of (i) $Pd_{17}Se_{15}$, (ii) Pd_7Se_4 , (iii) Pd_4Se and (iv) Pt, (b) LSV of bare Toray carbon in 0.5M H₂SO₄ at a scan rate of 2 mV/s. It may be noted that the currents are very small compared to the palladium selenide electrodes.

Hydrogen evolution mechanism

The mechanism of H_2 evolution involves multi-step process¹⁶ with the first step being the formation of H_{ads} .

$$H_3O^+ + e^- \rightarrow H_{ads} + H_2O$$

Subsequently, the formation of H_2 , may occur via one of the two different reaction pathways. First is the combination reaction (Tafel), in which two absorbed hydrogen atoms combine on the catalyst surface and other is based on the ion / atom reaction as given below (Heyrovsky step).

$$H_{ads} + H_{ads} \rightarrow H_2$$
$$H_3O^+ + e^- + H_{ads} \rightarrow H_2 + H_2O$$



Fig. S12. Impedance spectra on the three electrodes on Pd_7Se_4 , $Pd_{17}Se_{15}$ and Pd_4Se at the onset potentials over a frequency range from 100 kHz to 0.01 Hz. The equivalent circuit used to fit the data is also given. The circuits correspond to $Pd_{17}Se_{15}$, Pd_7Se_4 (a), and Pd_4Se (b) Electrochemical impedance spectroscopy (EIS) measurements reveal one semicircle in the case of $Pd_{17}Se_{15}$ and Pd_7Se_4 while a second semicircle is also observed on the Pd_4Se phase.



Fig. S13. Currents at different applied potentials as a function of number of cycles for $Pd_{17}Se_{15}$ and Pd_7Se_4 .



Fig. S14. XRD patterns of (a) Toray carbon, (b) $Pd_{17}Se_{15}$ and (c) Pd_7Se_4 before and after 3000 cycles of HER at scan rate of 100 mV/s.



Fig. S15. SEM image of (a) TC, (b) $Pd_{17}Se_{15}$, (c) Pd_7Se_4 and (d) Pd_4Se after running LSV for 3000 cycles [inset shows EDAX bar diagrams], (e), (f) and (g) shows the high magnification images of $Pd_{17}Se_{15}$, Pd_7Se_4 and Pd_4Se on toray carbon respectively.



Fig. S16. Cu under potential deposition (UPD) stripping voltammograms on Pd (a), $Pd_{17}Se_{15}$ (b), Pd_7Se_4 (c) and Pd_4Se (d) in 0.5 M H_2SO_4 + 2 mM CuSO₄ saturated with nitrogen recorded at a sweep rate of 20 mV/s. Respective background voltammograms at the same scan rate without CuSO₄ are also shown.

Methodology:

DFT calculations were carried out using CASTEP 6 code available within the Materials Studio suite. All the extended structure calculations were performed with plane wave basis truncated at a kinetic energy of 330eV. Both Local Density Approximation(LDA) with Ceperley and Alder^{1,2} data as parameterized by Perdew and Zunger (CA-PZ) along with non-local corrected generalized gradient approximation were used. Vanderbilt ultrasoft pseudo potentials and Monkhorst–Pack k-point³ mesh with seperation between k-points set at 0.5Å was used with cutoff of 5.0e⁻⁶ eV/atom for energy and 0.01 eV/Å for forces. Hirshfeld charge anaylsis were performed using CASTEP package.

Single point energy calculations were performed from first-principle within the framework of DFT employing Vienna Abinitio Simulation Package (VASP 5.3) utilizing a plane-wave basis and periodic boundary conditions and PAW pseudo potential.^{4,5} The Brillouin zone sampling was performed using a-centred Monkhorst-Pack mesh $3\times3\times3$ (Pd₄Se) (2×3×4) Pd₇Se₄ and (3×3×3) Pd₁₇Se₁₅.

Band structure:

All the three systems show metallic nature as shown in the figures S17 and S18. Among the phases, $Pd_{17}Se_{15}$ is more metallic than the other two and is also corroborated by experimental i-v measurements. Pd_4Se shows that the bands are degenerate throughout except between M to Gamma, Z to R and X to G points. Similarly, in the case of Pd_7Se_4 from gamma to T band show non-degeneracy and other paths fall in to doubly degenerate. In $Pd_{17}Se_{15}$, non-degenerate and double degenerate bands together are found in the frontier.

The projected density of states (DOS) of individual atoms performed using VASP software, illustrates that in Pd₄Se, the Pd atom population lies at the Fermi level. The selenium atom contribution at the Fermi level is almost nil. Projected orbital analysis also

shows that it is populated by the palladium d-orbitals. In the case of Pd_7Se_4 , the Pd atom population is found to be high at the valance band region. The Se atom contribution starts to show up as well. The DOS for $Pd_{17}Se_{15}$ shows that the contribution by selenium is considerable at the Fermi energy and Pd contributes below Fermi energy.

Charge density analysis:

Hirshfeld charge analysis is performed in CASTEP package for all three phases, The charge of Pd atom increases gradually from Pd₄Se to Pd₇Se₄ to Pd₁₇Se₁₅.



Fig. S17. Band structure of Pd₄Se, Pd₇Se₄ and Pd₁₇Se₁₅ (from left to right). The details of parameters used for calculations are given above.



Fig. S18. The projected density of states of palladium and selenium atoms in Pd_4Se , Pd_7Se_4 and $Pd_{17}Se_{15}$ phases (from left to right).



Fig. S19. XRD pattern of Pd_4Se before (i) and after (ii) 1000 cyclic voltammograms in presence of 1M KOH (a) and 1M NaOH (b) electrolytes.



Fig. S20. High resolution XPS spectra of Pd-3p (a), deconvoluted Pd- $3p_{3/2}$ region before (b) and after (c) stability test of Pd₄Se in 1M KOH electrolyte.



Fig. 21. C-1s deconvoluted XPS spectra of before (a), and after (b) etching the Pd₄Se film.



Fig. 22. High resolution XPS spectra of (a) Survey, (b) C-1s, (c) Pd-3d and (d) Se-3d, before (black) and after (pink) etching the Pd₄Se film.

Mole Pd(OAc	e ratio e)2 :RSeR	Phase formed		
1	1	Pd ₇ Se ₄		
2	1	Pd ₇ Se ₄		
		Pd ₄ Se		
3	1	Pd ₇ Se ₄		
		Pd ₄ Se		
4	1	Pd ₄ Se		
1	2	Pd ₁₇ Se ₁₅		
1	3	Pd ₁₇ Se ₁₅		
1	4	Pd ₁₇ Se ₁₅		

Table S2. (a) Binding energy values of Pd-3d peak and (b) Se-3d peak in different palladium selenide phases.

Material	Peak position (lower region)	Peak position (higher			
	(eV)	region) (eV)			
Pd ₁₇ Se ₁₅	336.2	341.4			
Pd ₇ Se ₄	335.7	340.9			
Pd ₄ Se	335.3	340.5			
	Material $Pd_{17}Se_{15}$ Pd_7Se_4 Pd_4Se	MaterialPeak position (lower region) (eV)Pd17Se15336.2Pd7Se4335.7Pd4Se335.3			

(b)

Material	Lower region (eV)	Higher region (eV)		
$Pd_{17}Se_{15}$	54.4	55.2		
Pd ₇ Se ₄	54.5	55.5		
Pd ₄ Se	54.3	55.4		

The atomic ratios of the elements obtained from XPS data.

Material	Pd/Se ratio
Pd ₁₇ Se ₁₅	1.3
Pd7Se4	1.9
Pd ₄ Se	4.1

Quantitative XPS analysis

The amount of palladium and selenium (Pd/Se ratio) present in Pd₁₇Se₁₅, Pd₇Se₄

and Pd₄Se materials is quantified using the following equation

 $Pd/Se = (I_{Pd} * F_{Se}) / (I_{Se} * F_{Pd})$

where,

 $I_{Pd} \mbox{ and } I_{Se}$ are the areas under the peaks for Pd-3d and Se-3d respectively.

 F_{Pd} and F_{Se} are the relative sensitivity factors (R.S.F) for Pd-3d and Se-3d respectively.

R.S.F of Pd-3d = 4.6

R.S.F of Se-3d = 0.67

Material	Pd-3d _{5/2} (eV)	O-1s (eV)	Pd-3p _{3/2} (eV)	Pd-3p _{1/2} (eV)
Pd	335.0	-	532.1	559.8
PdO	336.9	529.8-530.1	534.2	561.9
PdO ₂	338.6	-	-	-
O _{ads} layer on Pd	-	530.37	-	-
Pd ₅ O ₄	-	528.9-529.5	-	-
Dissolved O	-	528.98	-	-

(c) Binding energy values of Pd and O in different materials.

Table S3. Comparison of activities of the palladium selenide phases with other reported catalysts.

Catalyst	Catalyst loading/µg cm ⁻²	j ₀ / A cm ⁻²	Tafel slope / mV dec ⁻¹	TOF / s ⁻¹	j at η =150 mV (mAcm ⁻²)	Reference
Pd₄Se	200	2.3x10 ⁻⁴	50	0.47(η=50 mV)	16	Present work
Pd ₇ Se ₄	200	2.5x10 ⁻⁵	56	0.35(η =50 mV)	10	Present work
Pd ₁₇ Se ₁₅	140	6.6x10 ⁻⁶	57	0.2(η =50 mV)	3	Present work
Ni ₂ P	1000	3.3x10 ⁻⁵	46	0.015(η =100 mV)	20(η =130)	19
MoS ₃ /CNT composite	510	1.3x10 ⁻⁷	40	-	1.12	18
FeP/GSs composite	280	1.2x10 ⁻⁴	50	-	10(η =123)	19
Mo ₂ C-G composite	800	2.5x10 ⁻⁵	57	0.041(η =0 mV)	10	18

Table S4. Parameters obtained from equivalent circuit simulation of experimental impedance data.

Material	R _s	R _{ct}	C _{dl}	W	R _{ct1}	C _{dl}
Pd ₁₇ Se ₁₅	3	780.6	0.00035	0.0084 -		-
Pd ₇ Se ₄	2.2	100.1	0.0019	0.013	-	-
Pd ₄ Se	2.3	86.3	0.02	0.013	4.9	0.00029

Table S5. Hirshfeld charge analyses performed in CASTEP package using plane wave basis set (LDA/CA-PZ) for all three phases and are listed for different palladium atoms in different phases.

Hirshfeld analysis								
Pd ₄ Se			Pd ₇ Se ₄			P ₁₇ Se ₁₅		
Species	Ion	Hirshfeld charge (e)	Species	Ion	Hirshfeld charge (e)	Species	Ion	Hirshfeld charge (e)
Pd	1	0.05	Pd	1	0.13	Pd	1	0.16
			Pd	2	0.14	Pd	2	0.18
			Pd	3	0.07	Pd	3	0.17
			Pd	4	0.11	Pd	4	0.27

References:

- 1 P. E. Blochl, Phys. Rev. B: Condens. Matter Mater. Phys., 1994, 50, 17953.
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Calculation of thermodynamic potential

As for the thermodynamic potential of the reaction, selenide to selenate $(Se^{2-} \rightarrow SeO_4^{2-})$, we have used two methods to obtain this value.

In the first method, the standard reduction potential values of related reactions from the literature are used along with the free energy change (ΔG) to get the standard potential value of the desired reaction.

$$SeO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SeO_3 + H_2O \tag{1}$$

$$H_2 SeO_3 + 4H^+ + 4e^- \rightarrow Se + 3H_2O \tag{2}$$

$$Se + 2e^- \rightarrow Se^{-2}$$
 (3)

$$SeO_4^{2-} + 8H^+ + 8e^- \rightarrow Se^{2-} + 4H_2O$$
 (4)

The standard reduction potentials of the reactions 1-3 are 1.15 V, 0.74 V and -0.92 V respectively and the value obtained for the reaction (4) is 1.253 V.

In the second method, we used the equilibrium constant (K) value reported in the literature^a for the reaction and the reduction potential obtained is 1.315 V.

$$SeO_4^{2-} + 8e^- + 8H^+ \Leftrightarrow Se^{2-} + 4H_2O$$
 $\log(K) = 66.24$

a. M. A. Elrashidi, D. C. Adriano, S. M. Workman and W. L. Lindsay, Chemical-Equilibria of Selenium in Soils-a Theoretical Development, *Soil Sci.*, 1987, **144**, 141.

The difference may be due to the experimental values of K reported. It is clear that the oxidation of selenide to selenate occurs at potentials beyond the range studied. In addition,

overpotential will have to be taken in to account as well. Thus, the formation of selenate is ruled out in the present studies.